Feasibility of Ti-alloy Deoxidation by Reactive Slag Remelting

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Abstract

Titanium Aluminide intermetallics offer great mechanical properties at low density, beneficial for various mobile and stationary turbine applications. At the present development stage TiAl parts are manufactured by investment casting routes with comparatively low processing-yields. The generated scrap is mainly contaminated by oxygen uptake from ceramic moulds, runners and feeders. For mass-application of these materials in sectors like the automotive field, substantial cost-reduction of the raw-material will be crucial and can be achieved by efficient recycling of production scrap. The special thermochemical and kinetic characteristics of pressure electroslag remelting (PESR) show high potential to apply this process for the refining of titanium alloys as part of a process-chain recently designed in Aachen. Combined with vacuum induction melting (VIM) and vacuum arc remelting (VAR), PESR offers improved material quality at only slightly higher cost. The evaluation of material quality on one hand and cost structure for the whole process chain on the other is the major input of this paper to prove the feasibility of deoxidation of TiAl scraps by PESR.

1 Introduction

Efficiency improvements in turbo-systems applied in the power-, aerospace or automotive sector, demand increasing operating temperatures and pressures while at the same time engine designers aim to decrease the total mass of turning parts. Titanium-Aluminium based intermetallic alloys, deliver high temperature stability at comparably low density. They belong to a new generation of high-tech materials aimed for application on this sector. Even after 50 years of intensive alloy development, these materials are still considered to be *potential* high performance materials and introduction into mass markets has still not been achieved. Apart from the poor room temperature ductility and fracture toughness in comparison with other metallic structural materials, the slow technical application can be mainly contributed to the tremendous cost for the production of these alloys and their manufacturing.

Apart from metallic homogeneity of the produced ingots and the avoidance of non-metallic inclusions and segregations, one major factor for material quality is the absence of interstitial impurities. This is especially critical with regard to the tremendous affinity of titanium for oxygen and nitrogen. At the present stage of development the sum of interstitial elements is limited to 1,000 ppm. According to Güther[11] the upper limits for interstitials in TiAl are < 800 ppm for oxygen, < 200 ppm for nitrogen and < 200 ppm for carbon. In this sense γ-TiAl alloys have quality requirements largely twice as tough as for other Ti alloys presently applied like Ti6Al4V (Grade 5) with upper of oxygen < 2,000 ppm, nitrogen < 500 ppm and carbon < 800 ppm.

At present γ-TiAl alloys are being produced along the classic process chain for titanium alloys by vacuum arc remelting (VAR) of compressed metallic raw materials. It has been proposed by IME [8] that the production cost can be significantly reduced when TiAl is gained from aluminothermic reduction (ATR). Unfortunately these ATR-cast alloys show extremely high oxygen contents of about 1.5 wt%. Thus, recent activities at IME have been dedicated to find means for deoxidation of these alloys, with several process chains being evaluated at present. With regard to lowering oxygen levels, also Ti-scraps from turning and milling operations and TiAl-scraps from investment casting come into focus of a potential deoxidation process. Figure 1 shows the flowchart for integrated processing of primary and secondary TiAl materials presently under investigation in Aachen.

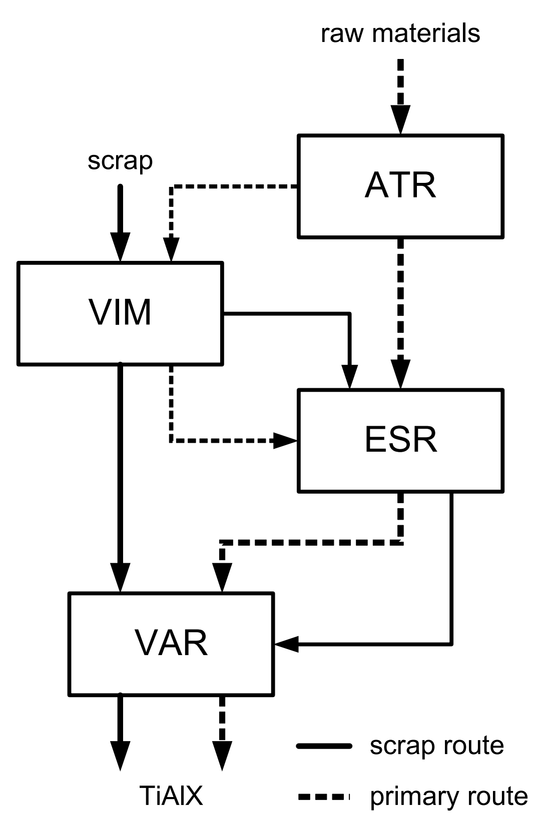

Figure 1: Process flowchart for the deoxidation treatment of virgin and recycled TiAl

In this concept both VIM and PESR show interesting potential for a deoxidation treatment, while VAR only offers very few chemical refining opportunities, apart from evaporation, which is not a feasible option for titanium. Oxygen dissolves in titanium in the form of TiO a comparatively stable oxide with a Gibbs free formation enthalpy (ΔG^0_f) of -513 kJ/mol and hence the removal of oxygen from titanium alloys is a challenging task. Simple degassing of Ti-metal in vacuum arc remelting (VAR) or electron beam melting (EBM) is not possible as it would require oxygen partial pressures below 10^{-14} Pa, for a binary γ-TiAl-system, the partial pressure still needs to be well below 10^{-8} Pa, a pressure impossible to reach in state-of-the-art vacuum melting equipment. In VIM a straightforward method for deoxidation is the charging of a calcium aluminium pre-alloy directly into the melt. When the solubility product between oxygen in the titanium melt and dissolved calcium is exceeded, CaO precipitates and floats on the melt. It can later be removed before casting as well as in subsequent VAR.

ESR for the remelting of pure titanium using CaF_2-based fluxes has been investigated by various researchers [1-3] with contradictory results concerning the properties of the final metal. Dissolution of metallic calcium in the flux and thereby deoxidation and purification of the remelted metal (e.g. removal of nitride inclusions) has recently been investigated by Ryabtsev et.al. [4] with promising results. A major challenge in the application of Ca-reactive slags in ESR lies in the evaporation of Ca at the melting temperatures of the titanium alloys. This effect can be kinetically suppressed by melting under inert gas overpressure, leading to pressure electroslag remelting (PESR) as a promising second alternative for deoxidation of recycled titanium aluminde scrap material.

3 Fundamentals

3.1 Melting and deoxidation in VIM

Melting of lumpy scrap and optional deoxidation takes place in a conventional vacuum induction furnace (VIM) using ceramic crucibles. Melting in VIM offers advantages for recycling processes like excellent chemical and thermal homogenisation of the melt due to inductive stirring, excellent heat control due to direct heating by induced eddy current, low gas/particle emissions and a high flexibility regarding shape, dimension, and number of input material, as well as the possibility for melt supervision, sampling and intermediate charging of reagents. However the choice to melt titanium scrap in VIM implies several challenges that have to be met by proper selection of crucible material, process window and post-processing. Titanium-containing melts pick up oxygen directly from any oxide-containing crucible material up to an equilibrium oxygen content in the melt, which depends on titanium activity in the melt and stability of the crucible oxide. At the same time the melt will be contaminated by the reduced metallic component of the refractories, and possibly by non metallic inclusions from mechanical wear on the lining. If direct deoxidation by a reducing metal is applied in VIM, dissolution of a surplus of this metal can be expected.

In order to evaluate the chemical and thermal stability of refractories, thermochemical modeling was applied [5] with the aim to calculate the oxygen content of liquid metal phases in thermochemical equilibrium with the crucible material as a function of process temperature T and melt composition. The total Gibbs energy minimiser FactSage^{TM} was applied along with the following reaction in order to find a material that gives a minimum of dissolved oxygen from its decomposition.

$$\alpha <Me_mO_n> + (X) = \alpha-\delta <Me_mO_n> + (XMe_{m\cdot\delta}O_{n\cdot\delta}) \qquad (1)$$

$<Me_mO_n>$ - solid crucible material (e.g. Al_2O_3), (X) - liquid Ti or Ti/TiAl alloy, δ - extent of reaction, δ $[0, \alpha]$

Thermochemical modelling for binary γ-TiAl (50 at% Al) and pure alumina (Al_2O_3) as crucible material predicts an equilibrium oxygen content of approximately 6,500 ppm slightly depending on the melting temperature. Calculation results predict significantly lower oxygen values (< 5,000 ppm) for CaO crucibles [5]. The electrodes for PESR deoxidation trials were thus cast from melts in pure prefabricated CaO crucibles.

3.2 Thermochemistry of deoxidation in ESR

The principle of ESR is based on the electrical resistance of slags as ionic conductors which allow for Joule heating on the application of electric currents in a water-cooled copper crucible. The tip of a consumable electrode dips into the slag and melts continuously while the metal droplets travel through the slag due to the difference in density. A liquid metal bath below the slag collects the droplets and through solidification the process continuously builds up an ingot with a controlled microstructure and smooth surface. Thermochemical calculations have shown that even the deoxidation of pure titanium, should be possible by electroslag remelting using reactive Ca-CaF_2-slags and inert gas atmospheres. Calcium is chosen as a reactant, because of its high oxygen affinity, reflected by a $\Delta G^0{}_f$ of -603 kJ/mol for the formation of CaO. The solubility product L_c of calcium and oxygen in titanium melts and its temperature dependency has been examined by Tsukihashi et al. [12]. They have developed a linear expression in the temperature range of 1,550°C to 1,750 °C and proven that deoxidation of TiAl by solution of calcium is feasible to levels below 500 ppm.

The principle of deoxidation by precipitation of CaO can be extended to ESR, using a Ca-CaF_2 melt according to equation (2) where subscripts below the elements in brackets indicate the phase in which the component appears to be dissolved. The equilibrium between the slag with dissolved metallic calcium and oxygen dissolved in the metal was previously examined by Okabe et al. [13], who also gave first experimental data on activities that apply for the slag metal equilibrium.

$$[TiO]_{TiAl} + [Ca]_{CaF_2} \Leftrightarrow [Ti]_{TiAl} + [CaO]_{CaF_2} \qquad (2)$$

As a main characteristic of the process only a partial volume of the total metal is in the molten state at any time of the process. This is unlike other metallurgical melting operations where usually the full load of a crucible is molten, allowing for mixing and homogenisation before casting.

To ensure a uniform oxygen content with respect to the full length of an ingot, the oxygen potential in the slag has to be carefully controlled during the whole melting process. Unfortunately, the slag enriches in CaO during the melt and is being depleted in calcium, hence thermochemical equilibrium will shift to the left side of equation (2), decreasing the effect of deoxidation over time. The result would be a non-homogeneous ingot in terms of oxygen content. Thus, calcium activity has to be continuously increased during the process to compensate this effect. Additionally the CaO-activity can be decreased by dilution trough the addition of CaF_2. Due to the current lack of reliable methods for online-measurement of these calcium can CaO activities in the slag under the harsh remelting conditions, the calcium content of the slag has to be controlled using mass-balance calculations and continuous feeding of deoxidation agents. Because the calcium vapour-pressure in the slag is near one atmosphere, also calcium evaporation has to be included in this calculation.

Furthermore the activities of the slag components in the system CaF_2-CaO-Ca have to be known in a broader range than given by Okabe. A calculation of the ternary system CaF_2-Ca-CaO was therefore conducted using the OptiSage-Module within FactSage^{TM} and applying a sublattice type model according to the Kohler-Toop approach, assuming that there was neither a tendency for near range ordering (like in silica melts where a quasi-chemical model is applied) nor a tendency for alloying (like in metal melts, where the compound energy formalism holds). The modeling according to Kohler-Toop was chosen instead of the Muggianu method because of better accuracy on the boundaries of the system. The model was further based on the eutectics and liquidus lines of the accepted binary systems Ca-CaF_2, Ca-CaO and CaF_2-CaO [7, 8].

Based on the calculated activities, the chemical equilibrium between oxygen in the metal and oxygen in the slag can be modeled in order to forecast the deoxidation efficiency of the metal phase as a simple function obtained by the least-squares method. It can be clearly expected that a desoxidation to lowest oxygen levels (< 100 ppm) can only be reached with extremely low CaO contents, while already 150 ppm oxygen should be possible throughout the full scale of CaO solubility of the slag by adjusting the Ca content. Figure 2 shows the necessary Ca-content for increasing CaO concentrations in the slag in the form of oxygen-equi-concentration-lines at different temperatures, for the deoxidation of a TiAl melt aiming on 480 ppm oxygen.

As previously presented by the present authors [10] the progress of deoxidation during an entire ESR melt was modeled as a function of slag composition and temperature. A calculation scheme was build up that assists in controlling the melt and adjusts slag composition for continuous deoxidation of γ-TiAl electrodes in PESR. A spreadsheet based on that scheme calculates the melting progress in discrete time steps and assumes chemical equilibrium for each step. It accounts for the solution of calcium in the metal, for the amount of calcium consumed for desoxidation, for the amount of calcium evaporated, for the increase of CaO concentration in the slag and successively for the necessary increase of metallic calcium concentration in the slag to compensate for the increasing oxygen potential of CaO.

This results in the calculation of an amount of calcium and CaF_2 to be charged for the next discrete melting step. The resulting composition and total mass of the slag are recursively fed back into the next melting step from where thermochemical calculations start again.

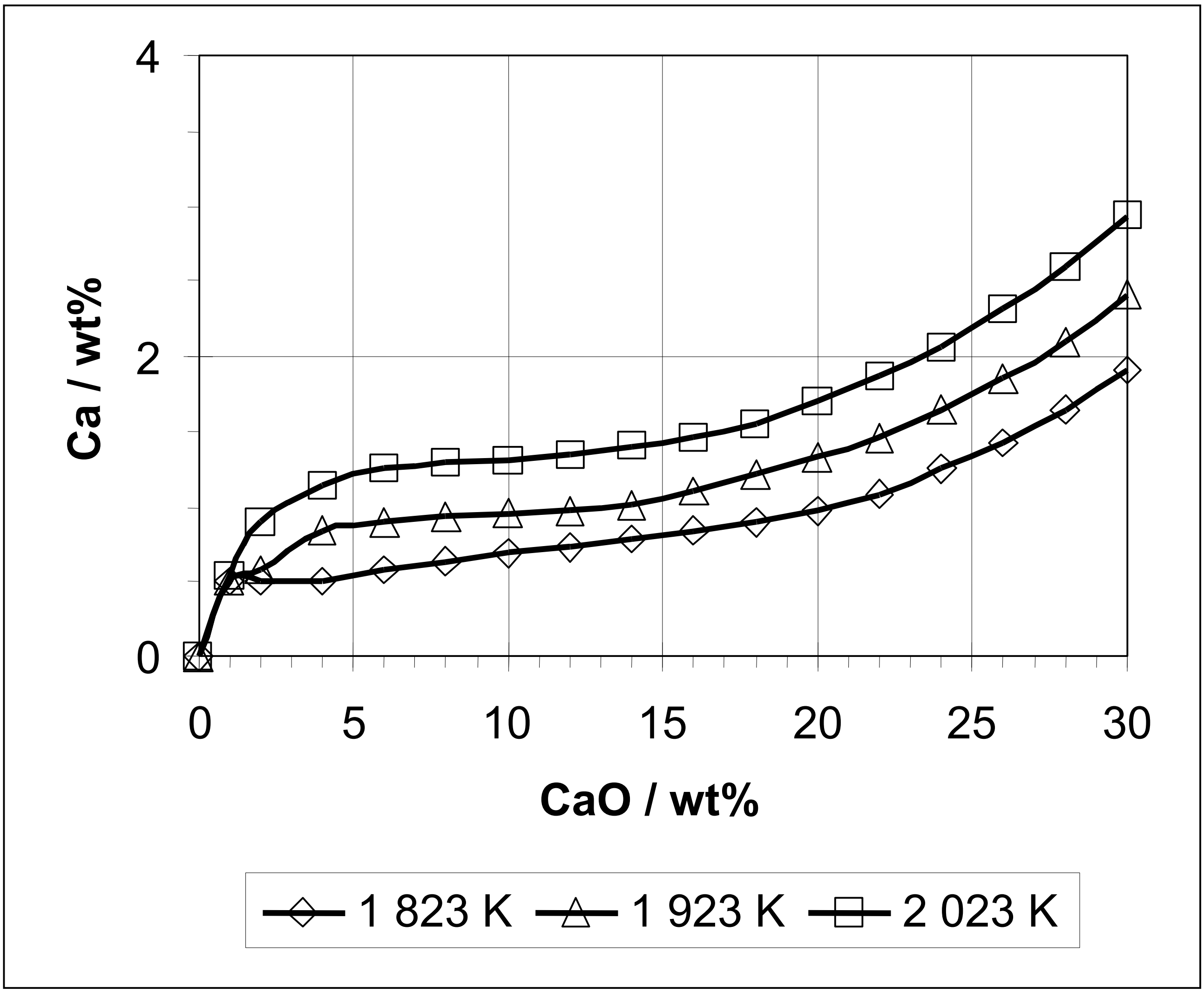

Figure 2: Necessary calcium content in the slag for maintaining constant reduction potential (lines of thermochemical equilibrium for an O content of 480 ppm in a γ-TiAl melt)

4 Experimental procedure

4.1 Characterisation of TiAl scrap material

As a first step in the recycling of metallic scraps, sampling of the input material plays an important role. Usually scrap input comes in batches of barrels or boxes and representative samples have to be prepared and analysed. The cost for this operation has been accounted for the economic evaluation of the entire processing chain. Trials for the present paper have been conducted on different kinds of sorted TiAl scrap, yet the feasibility of deoxidation via PESR has been assessed so far on used γ-TiAl sputter targets (Figure 3) of a close-to-binary composition.

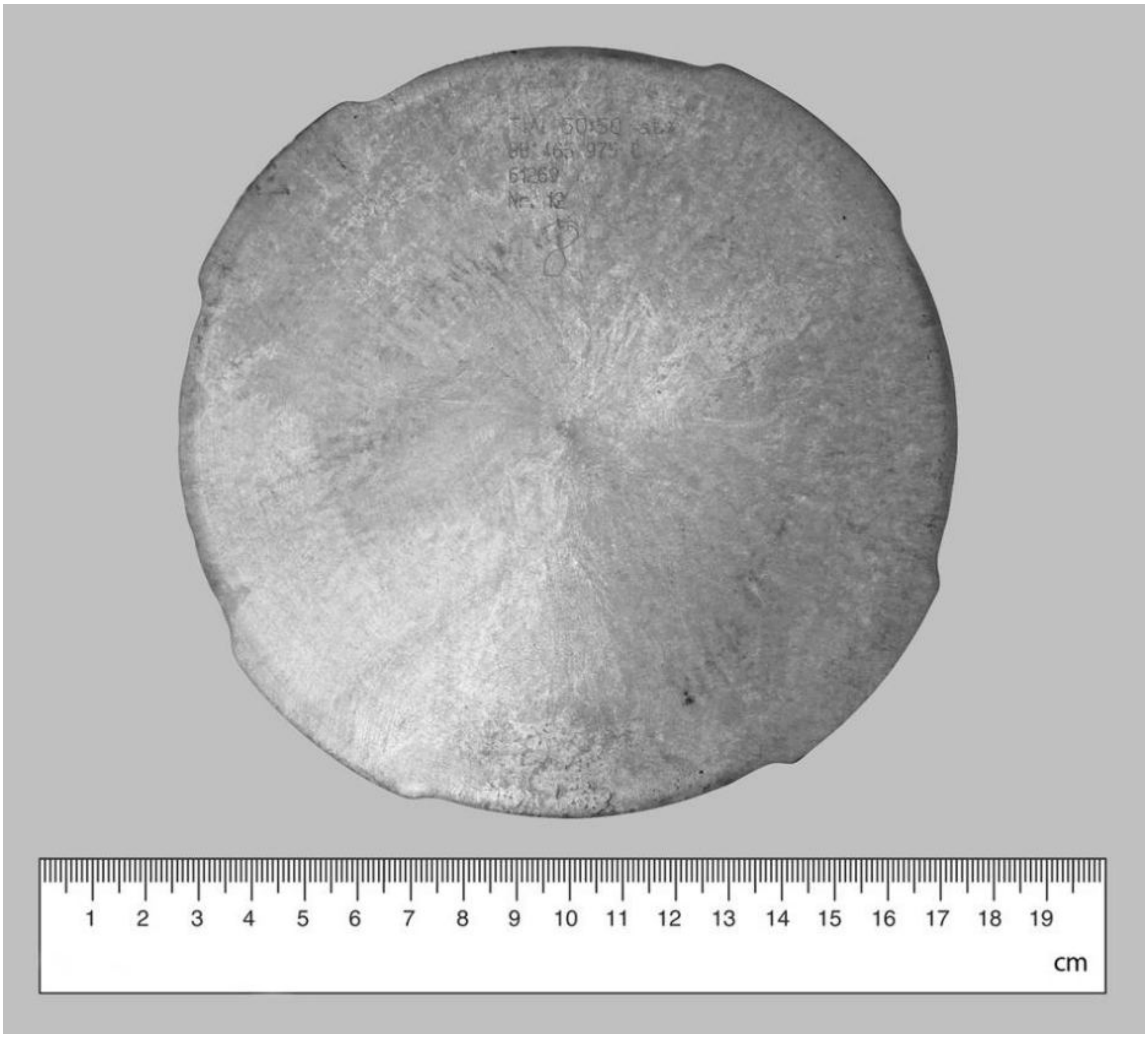

Figure 3: Sample of the TiAl target scrap

4.2 Preparation of electrodes by vacuum induction melting

Because of the tremendous reactivity of TiAl melts towards ceramic crucibles described above, special CaO crucibles were selected for consolidation of the scrapped TiAl targets. A chemical analysis of the crucible material shows very little contamination by other oxidic materials Table 1.

Table 1: Chemical analysis of VIM crucible material for remelting TiAl-scrap

Sample	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**
avg. wt%	99.28	0.14	0.07	0.05	0.48

The pilot scale melting trials were carried out, as reported in [5], using a vacuum induction furnace with a capacity of 100 kg steel and a nominal melting power of 150 kW. A crucible volume of 14 litres allowed a charge weight of 28 kg.

The material was charged into the crucible at room temperature, the furnace was then closed, evacuated below 10^{-3} hPa and flushed with argon twice to minimise the residual oxygen in the chamber. Melting took place under an argon pressure of 800 hPa to reduce the evaporation of refractory components or volatile alloying constituents. To avoid thermal shocks in the crucible, melting power was increased by degrees in steps of 10 kW every half hour. After detecting the first molten metal, the melting power was kept constant until all material was liquid.

For TiAl the casting temperature was set between 1,500 to 1,650 °C. Temperature measurements were carried out by immersion thermo-couples which were enclosed by a MMC casing. The homogeneous melt was cast into a water-cooled copper mould in order to obtain a segregation free electrode for ESR. Samples were taken in order to evaluate slag removal and deoxidization by subsequent PESR. Three electrodes have been prepared, resulting in the following compositions:

Table 2: Composition of the cast VIM electrodes made from TiAl-target scrap

Nr.	**Ti**	**Al**	**Fe**	**Si**	**Ca**	**Mg**	**O /ppm**
1	62.75 %	36.70 %	0.055 %	0.02 %	0.01 %	0.00 %	2,400
2	62.20 %	37.10 %	0.05 %	0.02 %	0.02 %	0.00 %	1,900
3	62.50 %	36.40 %	0.06 %	0.02 %	0.04 %	0.00 %	3,100

4.3 Deoxidation of electrodes by PESR

In order to test the calculated activities/activity coefficients and to prove the principle of PESR deoxidation for TiAl, four melts were conducted at varying pressures and varying calcium feed. The described electrodes cast from VIM were remelted at argon pressures of $1 \cdot 10^6$ and $2 \cdot 10^6$ Pa overpressure to examine again the influence of pressure on the calcium content in the slag. In terms of Ca/CaF_2 feed, the aim was to use the process control model previously presented. Parameters were plotted for the melting of the γ-TiAl-electrodes with a diameter of 110 mm and 800 mm in length and given oxygen content. The feed-rates suggested by the calculation were applied in the first trial. For the subsequent trials these rates were multiplied by 2 and 2.5 to achieve lowest possible deoxidation . In the initial calculation the ratio between CaF_2 and calcium in the feed was fixed to 4.1 as a good intermediate between calcium as a reactant and CaF_2 for dilution. This ratio was varied based on the assumption that eventually more calcium than calculated would evaporate from the melt i.e. excess Ca but not excess CaF_2 would be needed to achieve the necessary deoxidation. Table 3 gives an overview on the experimental plan. Note that electrode Nr. 3 was split upon two melts so in total four PESR melts could be conducted.

Melts were carried out in a pilot-scale PESR furnace (Leybold-Heraeus, now ALD) capable of operating under inert-gas overpressures up to $5 \cdot 10^6$ Pa. The furnace is equipped with a 5 kA/66 V power supply and modern monitoring and control systems. The ESR crucible used has a conical shape of 178 mm diameter at the base-plate and 159 mm at its rim and measures 880 mm in height. The initial CaO-content of the batch of WACKER 2052 slag (>97,5 % CaF_2) was determined to be 1.17 % by a titration method. For starting the process, a pile of welded chunks from target scrap was used to allow for proper heating and melting of the solid slag (Figure 4, left). In order to control the slag composition, the charging of additional slag and calcium was conducted during the processing time using calibrated screw feeders. The exact amount charged was double-checked after the trial by mass-balance on the material leftover in the slag bunkers.

Table 3: Experimental plan with variation in pressure and Ca feed rate

Trial code	**Type**	**initial O /ppm**	**Ca feed /g*min^{-1}**	**CaF_2/Ca**	**Factor on theory**	**P /10^6 Pa**
JR-ESU-01	binary γ-TiAl	2,400	5.1	4.1	1	1
JR-ESU-02	binary γ-TiAl	1,900	3.9	4.1	2	2
JR-ESU-03	binary γ-TiAl	3,100	6.11	3	2	2
JR-ESU-04	binary γ-TiAl	3,100	6.11	3	2.5	2

After the start-phase, operating power was melt-rate controlled in order to achieve a melting rate of 0.65 kg/min. For γ-TiAl this was achieved at a power supply of ~ 145-155 kW to the melt. Because of the low specific slag resistance, melting currents had to be set to 4,2 – 4,8 kA at 35-40 V. Immersion depth was controlled via a resistance and resistance swing controller. For melting under reactive (agitated) slag, the swing setpoint was allowed to be 7 mOhm at a total slag resistance of 8-10 mOhm.

4.4 Sampling and analysis

For evaluation of the deoxidation effect, preparation of micrographs and analysis on metallic elements samples were taken along a simple scheme (Figure 4 right). Because TiAl readily oxidizes special care has to be taken in all three steps, sampling, sample preparation and analytical method to avoid significant re-oxidation of the metal.

To decide whether the PESR process has achieved a homogenous deoxidation of the applied electrodes, wedges were cut from the ingot using a diamond saw. From these wedges, rectangular samples (40x30 mm) were prepared for XFA analysis of the metallic elements. The rest of the wedges were carefully crushed with a hammer into chunks of approximately 1 mm size as previous sampling investigations have shown lower oxygen values of crushed samples compared to drilled chips. For each oxygen analysis three randomly selected pieces were introduced in a Ströhlein ON-mat 8,500. Using the hot-gas extraction method and Ti6Al4 standards the mean oxygen content and standard deviation was determined. Right before hot-gas extraction the samples were treated with an etching solution (1:4:10 - HF:HNO_3:H_2O) in order to remove thin oxide layers. Previous results have shown that surface etching decreases the oxygen content analysed in the samples by 200 ppm in all analysed cases.

In parallel to metal analysis, slag samples were taken from the ingots' outer surface by peeling of slag in rings of 3 cm width. As the slag freezes on the crucible walls during the process, the composition at the respective process time can be conserved and later on examined. It is aimed to correlate slag composition to deoxidation effect in order to get additional information on the thermochemical equilibrium during the process.

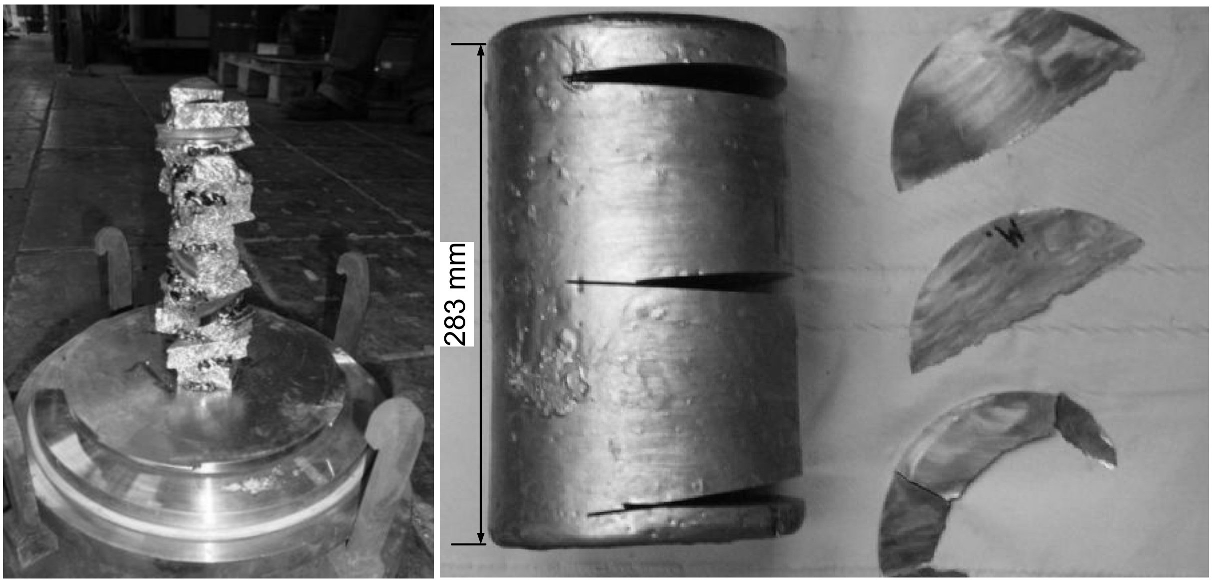

Figure 4: Pile of TiAl chunks for PESR start (left), sampling along the ingot axis (right)

5 Experimental Results

Figure 5 shows the log of the melting parameters applied on trial Nr. 2, with logging-time set to 1 s. After power is increased to 155 kW it can be observed that a constant melting rate of 0.75 kg/min is reached shortly after the start of the process and the linear ram travel ("Z") indicates stationary melting conditions. After the first minutes of constant melting, automatic melt rate control was applied which accounts for the continuous power decrease in the course of the melt. Pressure is slightly increasing due to the heating of the furnace atmosphere and the fact that all valves where closed during the trial. The measured resistance shows a relatively large "swing" compared to trials on steels and superalloys regularly conducted in the same furnace. This may be attributed to the fact of continuous charging and evaporation of calcium metal which leads to an agitated slag surface. During the start-up phase, large fluctuations in resistance are due to the process of melting the slag which takes place in a mixed regime of alternating electric arc and resistance heating, while variation during the final melting phase (hot-topping) is due to the increased resistance set-point at the end of the melt with the aim to minimise electrode immersion.

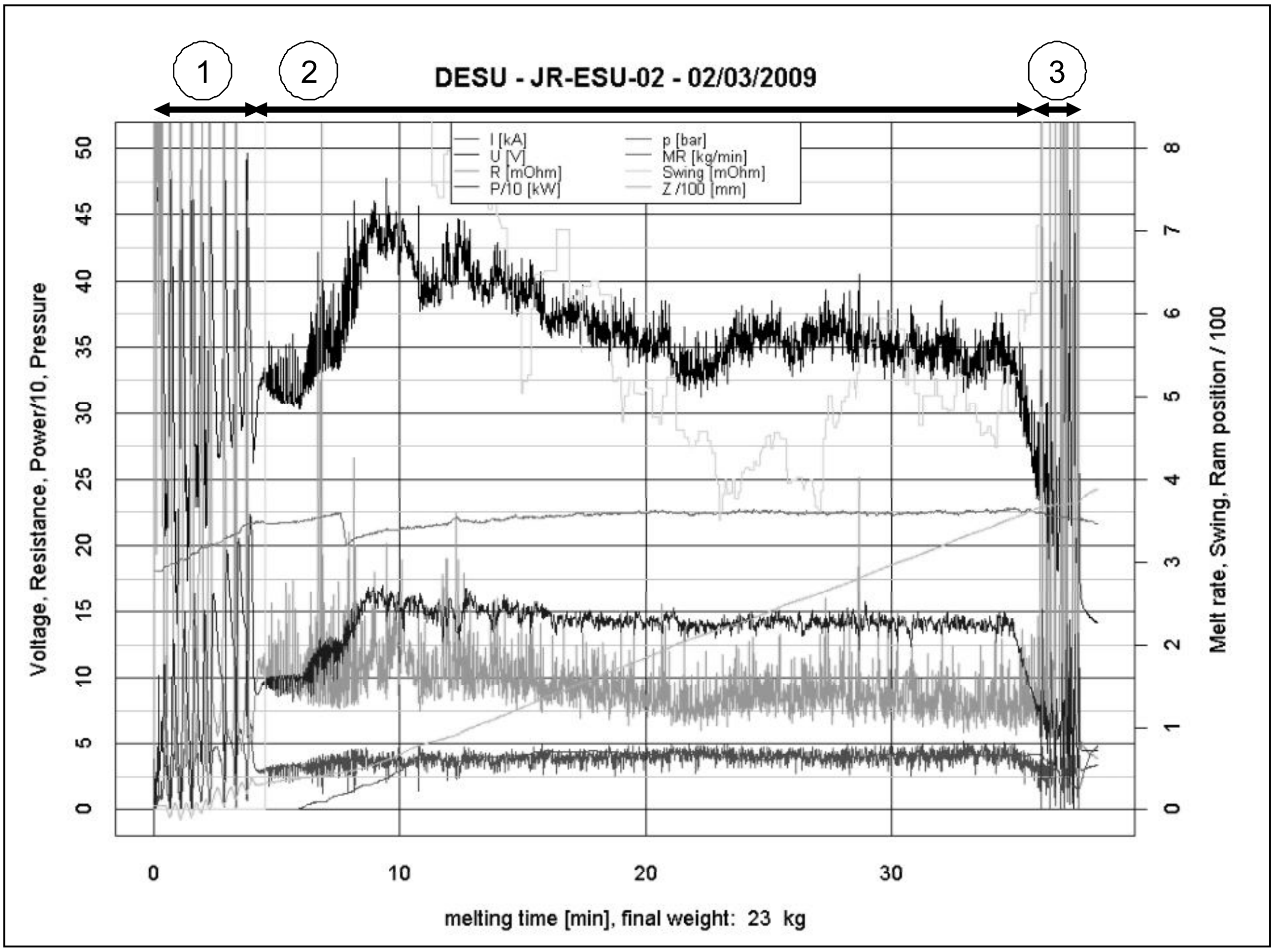

Figure 5: Melt-log of trial JR-ESU-02 shows constant melt rate but relatively high swing on slag resistance challenging melt control.
Phases: 1 – start-up, 2 – rate melt control, 3 - hot-topping

As a result of a hot-topping phase with minimised immersion depth the lower electrode surface after the trial appears to be almost horizontal. The immersion depth represented by the last slag level frozen on the electrode was in the range of millimetres (Figure 6). At present the first samples from trial Nr. 3 have been examined and show positive results in terms of a satisfactory deoxidation. An oxygen value of < 200 ppm could be achieved on the whole height of a 7 kg mini-ingot. A detailed presentation of the oxygen contents focussing on its homogeneity as well as on the distribution of metallic elements along the ingot axis will be presented at the conference, as chemical analyses are still outstanding.

Figure 6: Electrode leftover after PESR with reactive slag and obtained deoxidized TiAl-ingot

6 Economic Considerations

When the feasibility of deoxidation via PESR is examined, not only analytical results have to be taken into account. Compared to a processing route consisting of VIM including the deoxidation step and subsequent refining by VAR [6, 5] a three-step process with deoxidation via PESR may be more expensive. On the other hand the avoidance of deoxidation in VIM might reduce overall cost due to longer crucible lifetime, significantly reduced cleaning effort (working at higher pressures) and a higher yield of the deoxidation agent in the PESR slag system. Apart from that, PESR ingots may already achieve the necessary quality for their return into the manufacturing/casting route, hence a removal of inclusions is already managed by PESR and therefore it might not be necessary to include a second remelting by VAR.

To illustrate the three variants VIM + VAR, VIM + PESR and the triple melt VIM + PESR + VAR more precisely, a cost estimation project has been set-up based on the cost factors for material processing on the pilot-scale furnaces available at IME. It is assumed that this equipment operates on a daily one shift basis, giving rise to a theoretical annual treatment capacity of ~5 t or 220 melts. As major inputs to the calculation, prices of furnace equipment, scrap material and consumables have been collected in a literature research. Labour, energy and water consumption, yields etc. have been recorded during several experimental trials. Depreciation rates and overhead costs have been included according to available knowledge.

The cost structure (see Figure 7 right) for a triple melt calculation shows that ~25 % of total cost are attributed to labour, 36 % to depreciation and 22 % to consumables of which 2/3 would account for the scrap material which was assumed to have an arbitrary price of 8 €/kg. This might change dramatically as with larger production sizes labour intensity and depreciation cost will strongly decrease. It has to be noted that the calculated processing cost for the recycled γ-TiAl electrodes may only give indications and is not accurate enough for direct transfer to the processing cost in a potential industrial scale, nor may it be applicable to calculate a potential market price for recycled scrap material. The scale-up to a potential industrial plant is presently under consideration at IME. However, because the input parameters are comparable on all three processing alternatives, the results presented in Figure 7 (left) show a clear cost tendency of the alternative routes towards a two step process, which still have to be proven to be sufficient.

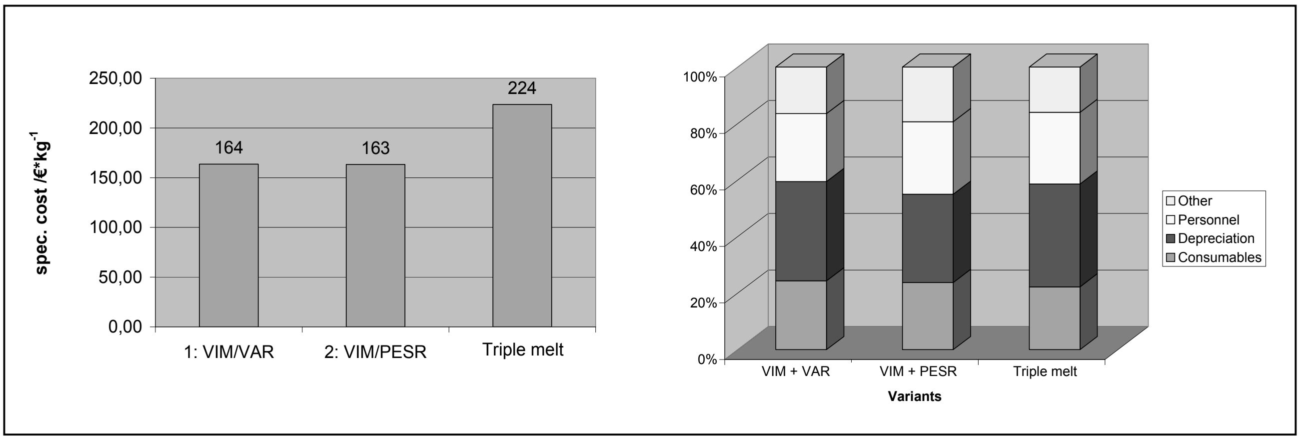

Figure 7: Results of a techno economic analysis show that deoxidation by PESR is not necessarily more expensive than the alternative VIM + VAR route.

7 Summary

PESR as a deoxidation process for Ti-alloys offers the opportunity to achieve lower oxygen contents at a reduced calcium consumption compared to VIM. However, it introduces some process-inherent challenges, such as the need for stationary melting conditions, both in terms of heat balance and chemical equilibrium. The thermochemical fundamentals for such process control have been carefully investigated. It has been shown experimentally that deoxidation via PESR is feasible and reaches levels below the specified 500 ppm oxygen, on the lower section of an examined ingot. Further analysis of metallic components and the process slag is currently underway. Detailed results will be presented at the conference. It can be clearly observed from economic calculations that deoxidation of TiAl scrap by PESR is competitive to the direct deoxidation via VIM and subsequent refining in VAR. Only if a third process stage must be involved, the cost per kg of treated material clearly increases due to a lower overall metal yield and increased effort.

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